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Liquid crystalline, rheological and thermal properties of konjac glucomannan

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Konjac glucomannan (KGM) exhibited liquid crystalline (LC) behaviour in aqueous solutions above 7% (w/w) concentrations as was determined by polarized optical microscopy and circular dichroism. The rheological properties of the concentrated LC solutions of KGM exhibited pseudoplastic behaviour. The fibrous extrudates retained a significant degree of flow-induced orientation as was determined by wide angle X-ray scattering, thereby indicating potential applications of KGM as fibres and films. Differential scanning calorimetry experiments showed that a significant degree of interaction occurred between KGM and water and that the KGM gels produced in our study cannot be classified as thermoreversible.

(Keywords: liquid crystalline behaviour; konjac glucomannan; rheological properties)

INTRODUCTION

Konjac mannan is a high molecular weight water-soluble non-ionic glucomannan found in tubers of the *Amorphophallus konjac* plant. Konjac glucomannan (KGM) is a linear random copolymer of (1 → 4) linked β-D-mannose and β-D-glucose. It has mannose and glucose units in a molar ratio of 1.6:1 with a low degree of acetyl groups (approximately 1 acetyl group per 17 residues) at the C-6 position[1,2]. The degree of water solubility is controlled by the presence of the acetyl units. *Figure 1* shows chemical structure of KGM as proposed by Maeda *et al.*[3].

KGM is not hydrolysed by digestive enzymes in human beings and is considered as an indigestible dietary fibre. However, it is hydrolysed by *Aerobacter mannanolyticus*[4] and is regarded as non-calorie food in Japan. The introduction of KGM in a high cholesterol diet reduced the total cholesterol levels in the liver possibly due to the absorption of cholesterol by KGM[5]. A more complete review of previous research concerning konjac glucomannan has been published[6] and will, therefore, not be included here.

A major problem concerning the thermal processing of polysaccharides is the strong interchain interactions which exist due to extensive hydrogen bonding. These interactions result in a polymer system which typically undergoes thermal decomposition before reaching its melting point. Thus, native polysaccharides are, in general, not processable by conventional thermoplastic methods without the use of water or an equivalent plasticizer.

The research on KGM so far has been limited to the isolation and characterization of the solution and bulk properties and the gelling behaviour, mainly for food applications[7–10]. In addition, KGM can be extruded into films for coatings and packaging applications. Processing of the KGM solutions from the liquid crystalline (LC) state can be very useful as the solidified product will retain the orientational molecular order, which will lead to improved stiffness and strength of the material. We have previously reported preliminary investigations of the LC behaviour[11] of KGM and blends with pullulan[12]. The primary objective of the present investigation is to examine the LC, rheological and thermal properties of KGM in aqueous solutions as a route to the identification of optimal processing conditions for this polymer.

EXPERIMENTAL

Materials

Nutricol® konjac was supplied by FMC Corporation and was further purified by following procedures given in the literature[13]. A 0.5% (w/w) solution of KGM was prepared in water and the solution was centrifuged to remove the insoluble material. The supernatant liquid was poured into an equal volume of methanol to precipitate KGM. The solid was then filtered, redispersed in water and freeze-dried. This yielded a fluffy white material, approximately 95% of the original powder, which was used for this study. The onset of decomposition and the decomposition temperature of KGM were *ca.* 250 and 330°C, respectively, as determined by thermogravimetric analysis. Certified grade Congo red was obtained from VWR Scientific and was used for circular dichroism experiments.

Sample Preparation

Different concentrations (C_p), ranging from 1–50% (w/w), of purified KGM solutions were prepared in small glass vials using a 0.1 wt% solution of sodium azide in

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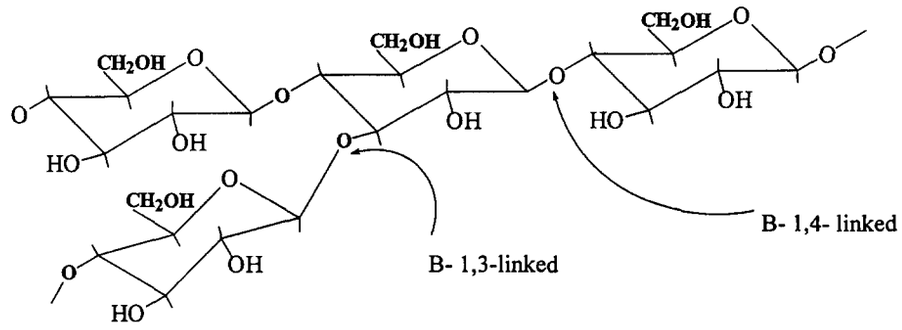


Figure 1 Structure of konjac glucomannan

distilled water. Sodium azide was used in the solutions to inhibit growth of microorganisms and did not inhibit chain–chain interactions or cause gelation as KGM is a non-ionic polysaccharide. Different concentrations of solutions containing KGM and the dye Congo red were prepared by mixing the polymer and 3×10^{-4} M dye solution. All the KGM solutions were allowed to equilibrate for about 1 month to prepare homogenous samples prior to analysis. The solutions were sandwiched between precleaned quartz plates to form the sample cells for polarized optical microscopy (POM) and circular dichroism study. The thickness of the cells was predetermined by using 20 μm glass beads and 50 μm thick mylar spacers between the quartz plates for dilute and concentrated solutions, respectively. The thickness of all the cells was later determined by a micrometer. The cells were sealed on all sides using epoxy to prevent water evaporation.

Films were prepared from isotropic and LC solutions of KGM by lightly spreading them using a Gardner knife over Teflon coated glass plates. In order to prepare the films at a slow rate of water evaporation, the solutions were covered with a petri dish. After film formation (usually 2–3 days), the films were dried at 80°C under vacuum before analysis.

Different concentrations (5–30%) of KGM solutions were prepared in water (containing 0.1% sodium azide) for the capillary rheometry experiments. In order to ensure homogenous mixing, the solutions were mixed using a twin screw extruder (C.W. Brabender) at room temperature. The samples were allowed to stand for approximately 4 weeks before the measurements in order to insure homogenous solutions.

Instrumental Methods

The number and average molecular weights of KGM were measured by gel permeation chromatography (GPC) using a Waters 600E system controller equipped with Shodex KB800 series columns, an RI detector (Waters, Model 410), DuPont Instruments column heating unit and a Waters Model 730 data module. Pullulan standards of narrow polydispersity (Polyscience Corporation) were used to construct a calibration curve from which molecular weights of KGM were calculated with no further correction. The mobile phase contained 0.3 M sodium sulfate and 0.05% wt/vol sodium azide.

The quartz cells were observed between polarized light using a Leitz Ortholux II microscope ($\times$ 320 magnification) equipped with a Mettler FP 50/52 hot stage. Circular dichroism (CD) spectra of the solutions in the quartz cells were recorded at room temperature using a Jasco J-710 spectropolarimeter under a nitrogen atmosphere. UV–VIS absorption spectra were recorded using a Perkin-Elmer 9 spectrophotometer.

Differential scanning calorimetry (DSC) experiments were performed using a Perkin-Elmer 7 Series thermal analysis system equipped with a low-temperature liquid nitrogen cooling apparatus. All the DSC scans were carried out under nitrogen purge at a heating and cooling rate of 10°C min^{-1}. The aluminum sample pans for the DSC measurements contained between 10 to 15 mg of the samples and were hermetically sealed. The dynamic viscoelastic properties of the KGM samples were determined using a Rheometrics mechanical spectrometer (RMS 605) at room temperature. All of the measurements were performed using a parallel plate geometry with a plate radius of 12.5 mm and a gap of 1.5 mm from 0.1–100 rad s^{-1} at a 20% strain rate.

The apparent viscosity measurements of the KGM solutions were carried out using a capillary rheometer (Goettfert) with a 15 mm piston diameter and a capillary length and diameter of 20 and 1 mm, respectively. The rheological measurements were conducted at three different temperatures (50, 70 and 90°C) and at six different shear rates varying from 100 to 5000 s^{-1}. Three runs were performed for each formulation and a pre-heat time of 240 s was allowed before each run. Uniform packing of the samples was achieved by maintaining a pressure of 8×10^5 bar during the pre-heat time. The fibrous extrudates of the KGM samples were collected at the end of each experiment and dried before characterization.

Wide angle X-ray scattering (WAXS) experiments of the KGM films and fibres were carried out using a Norelco vertical diffractometer equipped with a Bragg–Brentano focusing geometry, diffracted monochrometer and a CuK_α source. The diffraction patterns were recorded using 500 counts s^{-1} at a power setting of 35–40 kV and 15–20 mA.

RESULT AND DISCUSSION

Weight average molecular weight (MW) and polydispersity (MW/MN) of KGM were determined to be 3.9 and 1.9×10^6 g mole^{-1}, respectively, by GPC. These values are very similar to those obtained by earlier investigators[14–16]. However, the values are higher than those obtained by Clegg *et al.*[17] possibly due to their sonication procedure of the KGM solutions which may have dissolved some aggregates resulting in lower molecular weights. It should be noted that no alkaline salts were added and no heat was applied during the preparation of the KGM solutions in our study in order to avoid excessive gelation which may interfere with LC phase formation. Dilute solutions of KGM in water were formed for KGM concentrations of $\leq 2\%$ (w/w). In contrast for KGM solutions with concentrations $\geq 3\%$ (w/w), highly viscous aqueous sols were formed.

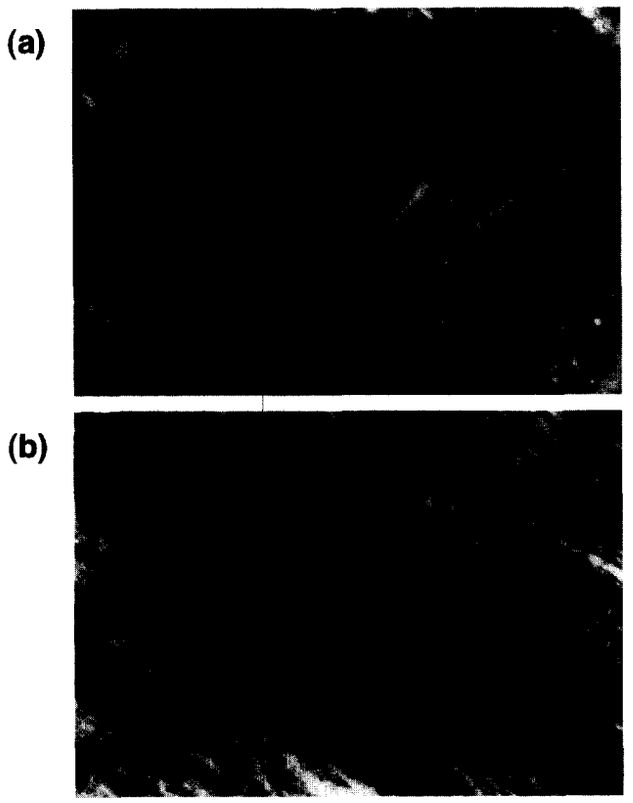


Figure 2 Polarized optical micrographs of KGM solutions: (a) 7% (w/w); (b) 10% (w/w)

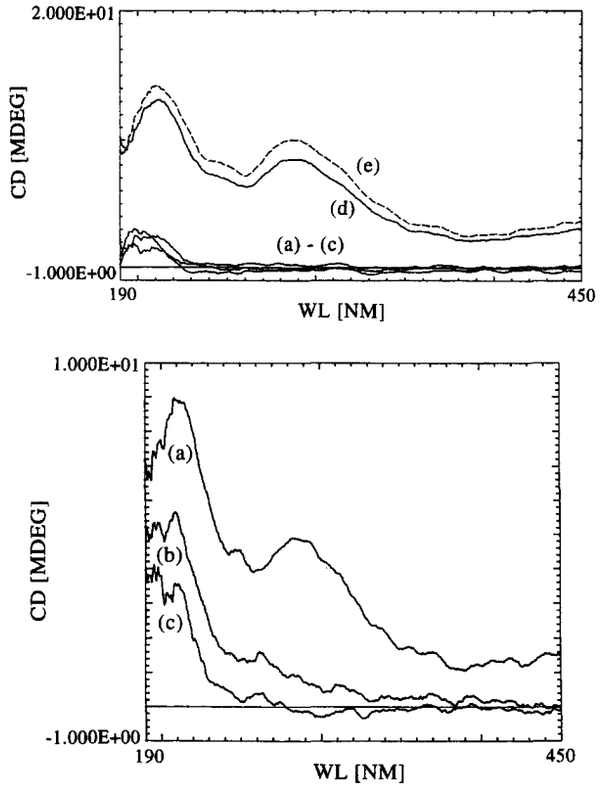


Figure 3 (a) CD spectra of KGM solutions perpendicular to the beam axis: (a) 1%; (b) 5%; (c) 7%; (d) 10%; and (e) 12%. (b) CD spectra of 10% KGM solution as a function of sample rotation: (a) perpendicular; (b) 45°; and (c) 90°

Liquid crystalline properties

Polarized optical microscopy (POM). The KGM solutions were sandwiched between quartz plates to form sample cells. The cells containing varying concentrations of solutions were examined under the microscope between crossed polarizers; however, no birefringence was detected until the concentration of $C_p = 5\%$ (w/w) was reached. A biphasic LC phase was observed at $C_p = 7\%$ (w/w) as shown in *Figure 2*(a). The samples showed a uniform LC texture at a concentration of 10% as observed in *Figure 2*(b). Therefore, the critical concentration (C_p') for KGM to display liquid crystalline behaviour in water is approximately 7% (w/w). As the KGM concentration increases, the dilute isotropic solution first undergoes a transition to viscous isotropic solutions and later, at higher concentrations, to anisotropic LC solutions. The cells of the anisotropic solutions (10 and 12%) were observed as a function of temperature at 5°C min^{-1} using the hot stage. No flow was observed and the anisotropy was retained when heated up to 80–90°C. Therefore, an order–disorder clearing transition did not occur in the KGM samples. There were limitations in studying temperatures higher than 100°C since water was the solvent. It should be noted that if the birefringence observed between the cross polarizers was due to any artefacts such as aggregates, the solutions would have been homogenized or deaggregated during the heating process using the hot stage. The retention of birefingence even after the heating process indicates that the anisotropy is due to the LC mesophase formation.

Circular dichroism (CD) measurements. CD Spectra (ellipticity) of the cells [$C_p = 1$, 5, 7, 10 and 12% (w/w)] were recorded in the wavelength region of 190–500 nm as a function of concentration at room temperature as shown in *Figure 3*(a). The cells were positioned perpendicular to the beam axis. The 1, 5 and 7% solutions did not exhibit a notable CD signal. When the sample concentration was increased to 10%, two positive CD bands appeared at approximately 210 and 290 nm with a tail in the visible wavelength region. The intensity of these bands increased with increasing mesophase concentrations (12%). This increase in the intensity of the CD bands with higher sample concentration indicated an increase in the ordering of the corresponding mesophases. These CD results are in agreement with the POM studies, and it seems that KGM forms a mesophase above 7% (w/w) concentration. However, it should be emphasized that the intensity of the CD signals for the KGM solutions were not very strong.

The CD spectra measurements that involve viscous or solid polymeric samples have the possibility of artefacts arising from the presence of stress-induced linear dichroism[18]. Linear dichroism and birefringent contributions in a CD spectrum can be eliminated by averaging spectra recorded at various sample positions as the sample is rotated about the beam axis. The average of such spectra is the true CD signal. During the preparation of the sample cells, high shear is invariably applied due to high viscosities of the KGM solutions. This may give rise to linear dichroism effects during the CD studies and may complicate data interpretation. In order to verify the influence of linear dichroism, CD measurements were conducted at different angles (relative to the beam axis) for the 10% sample cell as shown in *Figure 3*(b). It is observed that the CD band at 290 nm disappeared when the sample cell was rotated by 45 and 90°, but the intensity

of the band at 210 nm remained almost constant. This demonstrated that the CD bands at 210 and 290 nm were contributions from LC birefingence and linear dichroism, respectively.

Further optical characterization of the KGM LC solutions was conducted by UV–VIS absorption spectra from 190 to 450 nm. The spectra of 1% KGM solutions showed an absorption band at 210 nm and a weak band at 230 nm, and the 10% sample showed an absorption band at 210nm and a weak band at 275 nm. These bands correspond well with those observed in the CD measurements. However, there were no sharp selective reflections observed due to the LC phase formation in the spectra.

Direct CD studies of unmodified simple polysaccharides have been limited due to the absence of absorption bands within the wavelength range accessible with conventional instruments. Even though high optical rotations have been measured for the LC phase[19,20], no cholesteric reflections were observed for unmodified cellulose. The evidence of an ordered phase is based mainly on the shear-induced birefringence. CD bands were not observed for the most concentrated and anisotropic solutions of unmodified chitosan[21]. However, the LC solutions of phenyl isocyanate chitosan derivative showed strong positive CD and UV peaks at 238 nm which represented a cholesteric texture[21]. Strong CD bands were also observed in *N*-phthalolyl- and *N*-phthalolyl-acetyl chitosan derivatives due to the presence of phthaloyl chromophoric groups[22]. Therefore, direct optical studies of chiral polymers may require the presence of chromophores which will absorb radiation in the region of the spectrum accessible with conventional spectropolarimeters. When such chromophores are absent in polymers (e.g. simple polysaccharides), they can be added in the form of dyes which can bind to the polymer backbone without conducting any chemical modifications. When the conditions are appropriate the optically inactive dye, when dissolved in the polymer solutions, becomes optically active and shows a CD spectrum providing information about the chirality of the polymer chain. This is known as induced optical activity. Induced CD has been observed for Congo red, a direct dye, in regenerated LC cellulose films[23] and in solutions of methyl cellulose[24], $\beta(1 \rightarrow 3)$-D-glucan curdlan[25], amylose[26] and mannan[26]. Since the CD bands for LC solutions of KGM were not very strong, probably due to the absence of chromophoric groups, attempts were made to induce optical activity by dissolving Congo red dye in the solutions. CD spectra of the isotropic and anisotropic solutions containing Congo red dye showed bands at 210 and 290 nm, and were very similar to those shown in *Figure 3*(a). Weak UV–VIS bands were observed at 350 and 500 nm for the KGM solutions. In cases of regenerated cellulose films[23] and methyl cellulose solutions[24], strong positive CD bands were observed at 500 and 420 nm, respectively. Congo-red-induced optical activity for the cellulose films and methyl cellulose solution is mainly from the chain conformational effects and not from associations of the dye at chiral centres[24]. However, dye containing solutions of: (1) cellulose in dimethylacetamide–lithium chloride; (2) hydroxypropylcellulose in water; and (3) ethyl cellulose in dimethylacetamide do not show optical activity. Therefore, the dye binds only to some of the cellulose derivatives depending on their degree of substitution and substituents size. Thus it is possible that the presence of acetyl units and short branches at the C-6 and C-3 positions,respectively, may cause steric hindrance and prevent the dye from binding with the KGM backbone resulting in no induced optical activity. It may be possible to introduce chromophores on the KGM backbone by chemical modifications and this is the focus of our future work.

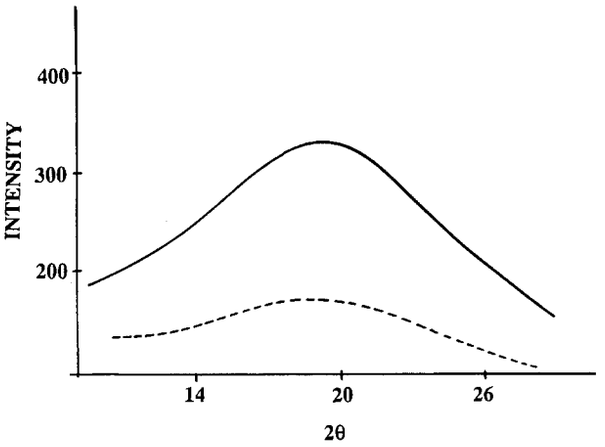


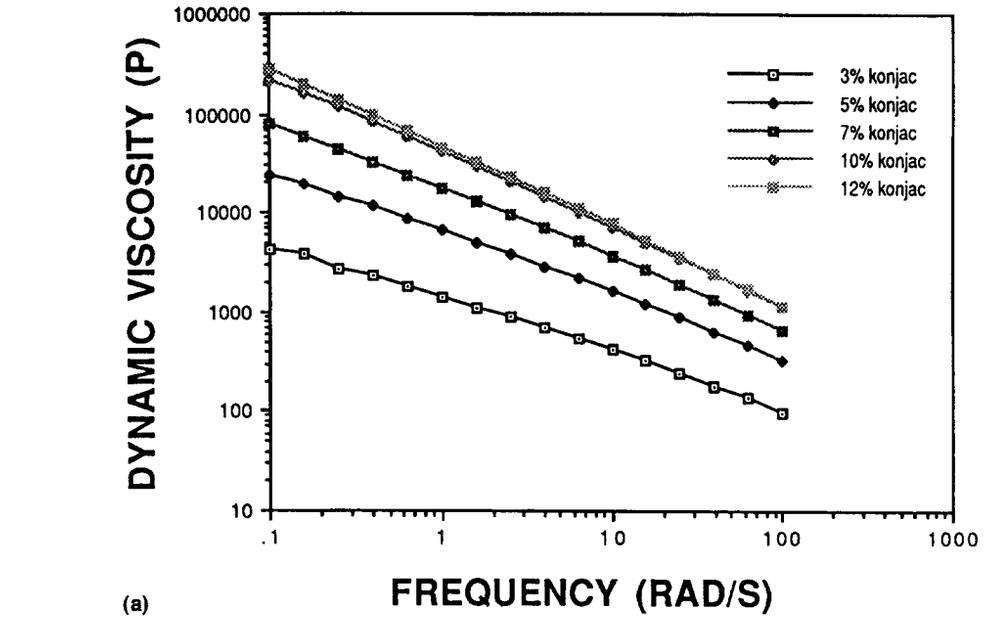
Figure 4 WAXS diffaction patterns of KGM films from different concentrations: 5% (- - -) 10% (———)

Wide angle X-ray scattering. Further evidence of mesophase formation was obtained from X-ray diffraction studies on films prepared from isotropic and anisotropic solutions of KGM. The film prepared from isotropic solutions [5% (w/w)] was transparent and did not show any birefringence when observed between cross polarizers of the optical microscope. However, the film prepared from anisotropic solution [10% (w/w)] was cloudy and highly birefringent when observed by POM. This indicated that the liquid crystalline cholesteric order was retained when the KGM films were cast from anisotropic solutions by slow evaporation as was observed for cellulose[23] and cellulose acetate butyrate[27].

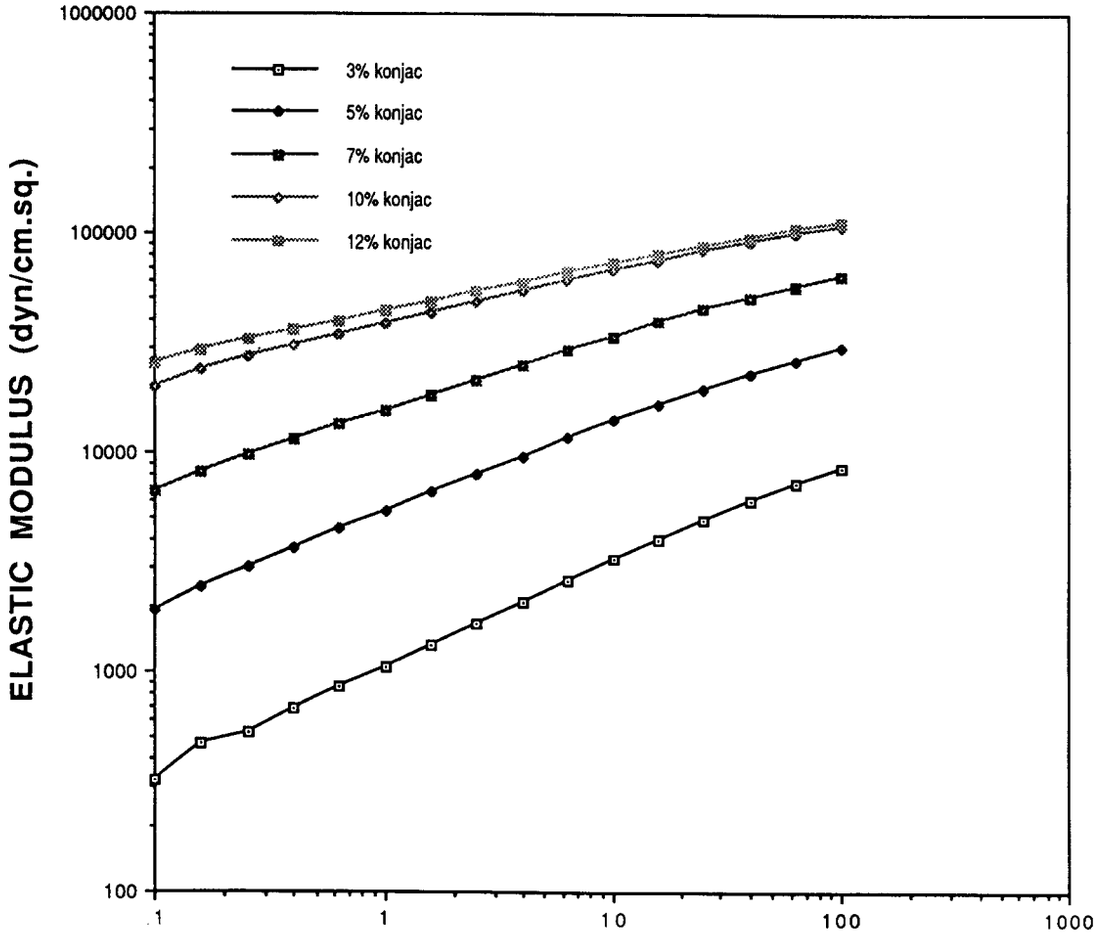
Figure 4 shows the X-ray diffraction patterns of the films prepared from isotropic and anisotropic solutions. The film from the isotropic solutions was almost amorphous (dotted line), but the film from liquid crystalline solution displayed a relative increase in crystallinity (solid line) with a broad diffused scattering at about 20° (2θ) which corresponds to $d = 4.57$ Å

Mesophase formation in polymers is mainly attributed to the backbone rigidity as has been observed for several polysaccharides. The value of α, in the M–H–S equation range from 0.5 for a Gaussian coil to 1.8 for rigid rods. The values of α for cellulose and cellulose derivatives range from 0.9 to 1.0 and classifies them as semi-rigid polymers.

The α values of the nitro-[28] and methyl-[15] KGM derivatives are from 0.95 to 0.75, respectively, and it shows that these derivatives are semi-rigid. In general, derivatization makes the polymeric backbone more flexible. Therefore, it can be presumed that the rigidity of unmodified KGM will be greater than its derivatives and most probably will have a higher α value. Semi-rigid polymers are better represented by the Kratky–Porod worm-like chain model rather than the random flight model and the chain stiffness is measured by its persistence length and the equivalent Kuhn segment length. Since several of the molecular parameters such as persistence length, diameter and the mean-square end-to-end distance of the unperturbed KGM chain are not determined, it is difficult to compare the experimental critical volume fraction [$C_p' = 7\%$ (w/w]



(a)



(b)

Figure 5 (a) Dynamic viscosity of KGM solutions as a function of frequency; (b) dynamic elastic modulus of KGM solutions as a function of frequency

value to that predicted by using Flory's equation[29]. Other umnodified polysaccharide such as schizophyllan formed cholesteric mesophase in aqueous solutions at concentrations above 10 wt% and it has a persistence length of about 1800 Å[30]. Since the LC mesophase formed at low concentrations (7 wt%), it seems that the persistence length of KGM is very large as its backbone is fairly rigid. If the molecular weigh of KGM is reduced then it is expected that the gelation may occur at higher concentrations and may allow the formation of an organized LC structure which will exhibit higher optical reflections. Since the reduction of molecular weight had a positive

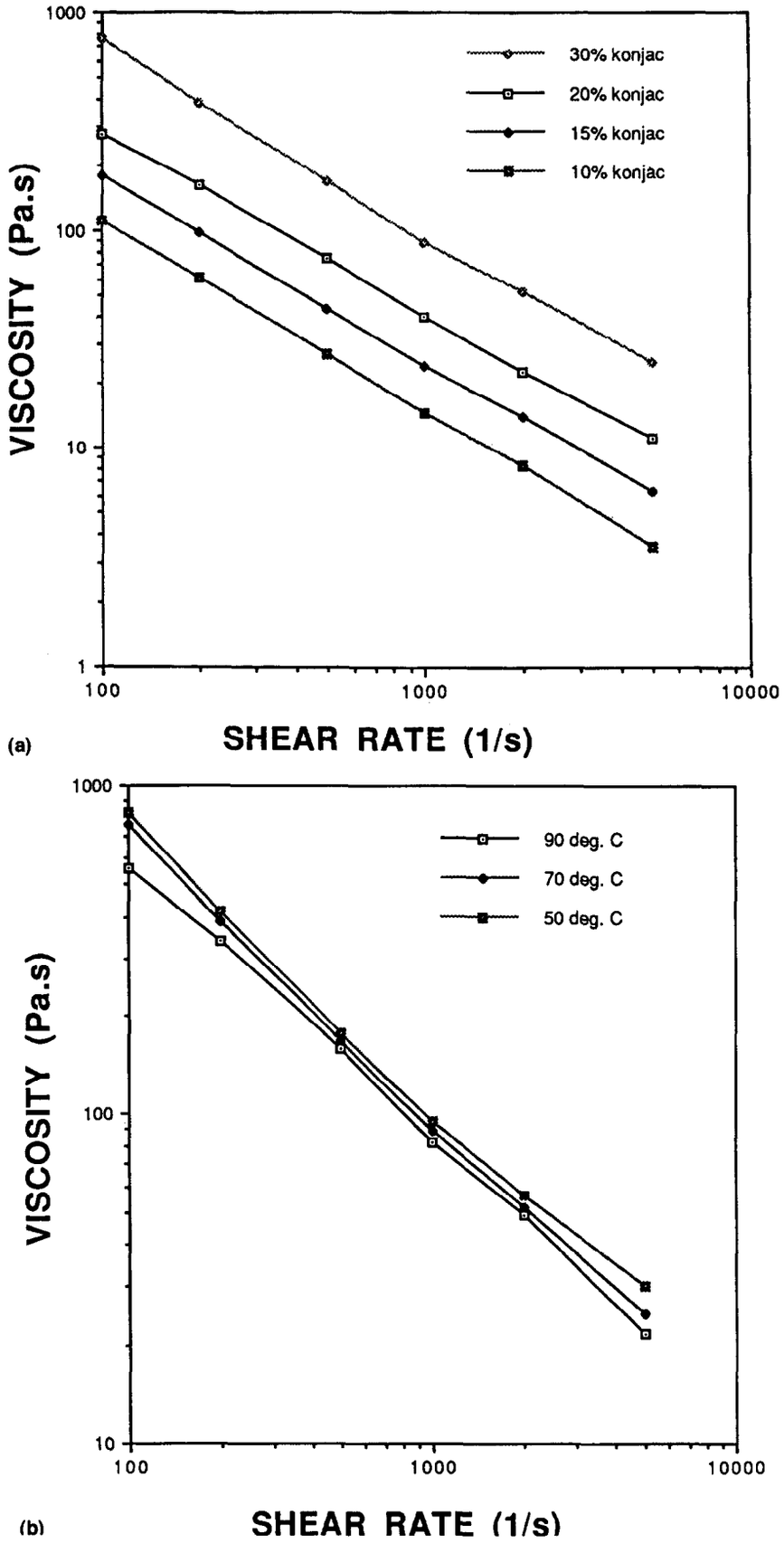


Figure 6 (a) Apparent viscosity of KGM solutions as a function of shear rates at 70°C; (b) apparent viscosity of 30% KGM solution at different temperatures

impact on the polymorphism of KGM[13], it is possible to improve the formation of a well-defined LC structure. However, the critical concentration will increase with a decrease in the molecular mass. Flexible side chains introduced on the KGM backbone by chemical modification may facilitate the orientation of the main chain by increasing its mobility which may prevent gelation from interfering with the LC phase formation. However, the

persistence length of the derivatives will be relatively low and the critical concentration will increase to higher values. In addition, these derivatives may not dissolve in aqueous solutions and organic solvents may be required to conduct the LC and rheological studies.

Rheological properties

Measurement at low shear rates. *Figure 5*(a) represents the dynamic shear viscosity as a function of frequency of the KGM solutions which were measured on the RMS rheometer at low deformations. The viscosity of the KGM samples increases with increasing concentration. However, the viscosity does not drop after the solutions become liquid crystalline, i.e. after 7% (w/w) as is commonly observed for other LC solutions of cellulose acetate[31], cellulose triacetate[32], cellulose acetate butyrates[33], hydroxypropylcellulose[34] and ethyl cellulose[35]. This can be due to the occurrence of gelation in the KGM solutions prior to the formation of the LC phase, which limits the development of an ordered structure. Shear thinning is observed for the KGM solutions. *Figure 5*(b) illustrates the dynamic elastic modulus (G') at different frequencies and concentrations of the KGM solutions. Similar to any viscoelastic material, G' values increase with frequency. The trend of G'' is very similar to that of G' (not shown). Typically, the mechanical spectrum of a strong gel consists of two horizontal lines of G' and G'' with a slight increase in the values at higher frequencies. However, weak gels are much more frequency dependent than the strong gels[36]. Based on this hypothesis, the KGM mechanical spectrum follows the trend of a weak gel. It is observed that as the concentration increases, the frequency dependence of the KGM solutions decreases, especially after 7% concentration. There appears to be a transformation from a weak gel to a relatively strong gel with a rise in concentration. Steady-state experiments are required to quantitatively distinguish the gel system. It would be interesting to conduct the rheological experiments as a function of salt content and solution concentration due to the occurrence of simultaneous competing events of gelation and LC phase formation.

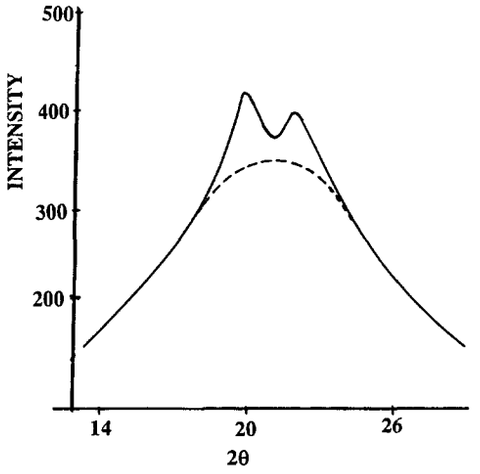


Figure 7 WAXS diffraction patterns of KGM fibers from different concentrations: 15% (- - -); 30% (———)

Rheological experiments of 1% KGM solutions containing potassium carbonate exhibited strong elastic gels[37]. G' and G'' values were almost independent of the frequency for the KGM/xanthan (70/30) mixed gels at 0.5% total concentration and represented strong gels[38]. It should be noted that the absolute values of these properties (G' and G'') were lower than those determined in our study due to higher KGM solutions concentrations used in our experiments.

Measurement at high shear rates. In order to optimize the processability of KGM using conventional melt processing methods, it is required to determine the rheological properties at high shear deformations. Experiments were conducted on 10–30% LC solutions of KGM from 50 to 90°C at different shear rates. *Figure 6*(a) represents the

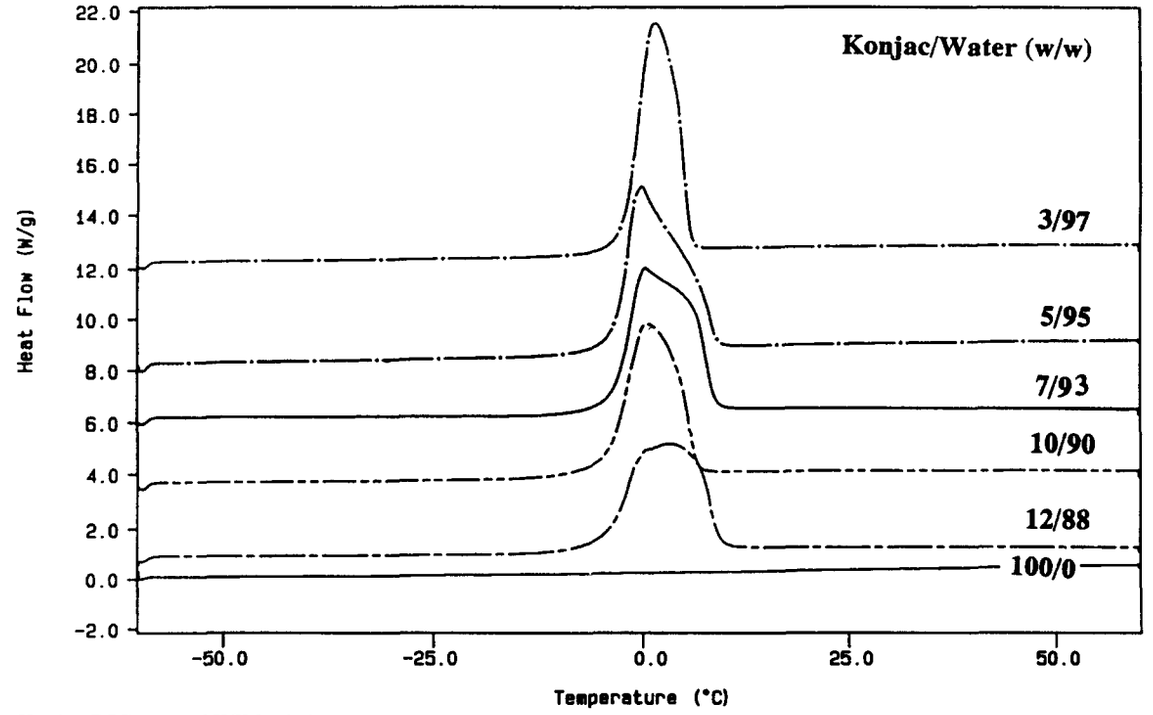


Figure 8 Heating DSC scans of KGM solutions

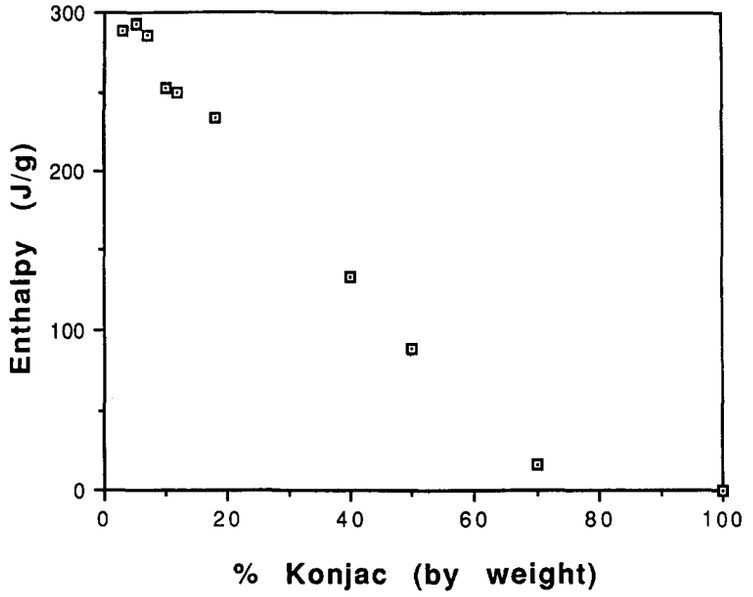


Figure 9 Heat of enthalpy of KGM solutions as a function of % KGM

apparent viscosity at varying shear rates of KGM solutions at different concentrations conducted at 70°C using a capillary rheometer. The viscosity of the KGM solutions decreases at higher shear rates and displays a shear thinning behaviour, which is commonly observed for thermoplastic polymers. Viscosity of the KGM solutions increased to a great extent with an increase in concentration from 10 to 30%. *Figure 6*(b) shows the viscosity of 30% KGM solutions as a function of temperature at varying shear rates. It is seen that the viscosity values do not seem to be a function of processing temperatures which is very surprising. A similar rheological behaviour was also observed for pullulan samples which were extruded using 15–30% of water as a plasticizer[39]. This may be due to some interactions between KGM and pullulan with water molecules. Analogous viscosity results were observed for other KGM solutions at different temperatures. KGM solutions can be processed at temperatures and concentrations ranging from 50–90°C and 10–30% concentration. The optimum processing conditions to prepare films or fibres appear to be with a 30% KGM solution.

Wide angle X-ray scattering. Figure 7 shows the WAXS diffraction patterns of the KGM fibres collected during the capillary rheometry measurements from 15 and 30% KGM solutions. It was difficult to collect fibres from isotropic solutions ($< 7\%$) due to the very low viscosity. The intensity of the WAXS pattern for the fibres form the 15% KGM solution is relatively higher and sharper when compared with those of the film (see *Figure 3*). This is possibly due to the orientation effects during the flow of the solutions through the capillary die. The fibres from the 30% solution (solid line) are more oriented than the ones from 15% KGM solution (dotted line). Sharp reflections are observed at $d = 4.57$ and 4.17 Å, which indicates that the fibres from the 30% solutions are more oriented. Similar values were also observed during the electron diffraction studies by Chanzy[13]. This may represent mannan II-type crystallization of the KGM fibres. This confirms that the liquid crystalline order in the solutions is preserved in the processed polymer and induces an ordered structure. This will presumably improve the physical properties of the fibres or films processed from the LC mesophase. Therefore, KGM represents a potential candidate for the fabrication of fibres, films and moulded materials with improved properties for various applications.

Thermal properties

Several DSC investigations on water–polysaccharide systems have been performed to study the types of water (non-freezing bound, freezing and free) as well as possibilities of gel–sol transitions and LC phases[40,41]. DSC data of the aqueous KGM samples upon heating and cooling were performed to investigate the phase transitions in the KGM–water system. *Figure 8* shows the nomalized heating scans of KGM–water ranging from 3–100% (w/w). The pure KGM sample has no phase transitions from −50 to60°C. Free (bulk) water exists in samples with as little as 3% KGM. The endotherms displayed upon heating are somewhat broad and structured for all the compositions, and the transition becomes broader at higher KGM concentrations. The structure indicates that there is water associated with KGM and this behaviour has also been typically observed in other water–polysaccharide systems[41,42]. In addition, the endotherms occur partially above 0°C, suggesting different KGM–water environments which may influence the motion and contribute to the melting behaviour. There were no LC gel–sol transitions observed in the heating scans for the LC solutions (i.e. above 7%). This is in agreement with the POM studies which showed no significant changes in the texture up to 80°C. Further studies are required to re-examine these transitions upon annealing and quenching as well as to quantitatively determine a phase transition diagram for the water–KGM system. There were no other endothermic transitions observed which could have represented the melting of the KGM, gels as observed for KGM[6,37], and mixed KGM gels[43–45] with other hydrocolloids in the presence of salts. Therefore, the KGM–water gels in our study are not thermoreversible.

The enthalpy of melting ($J\ g^{-1}$) as a function of % KGM is shown in *Figure 9*. ΔH is close to that of bulk water (i.e. $333\ J\ g^{-1}$) and zero at low and 100% KGM

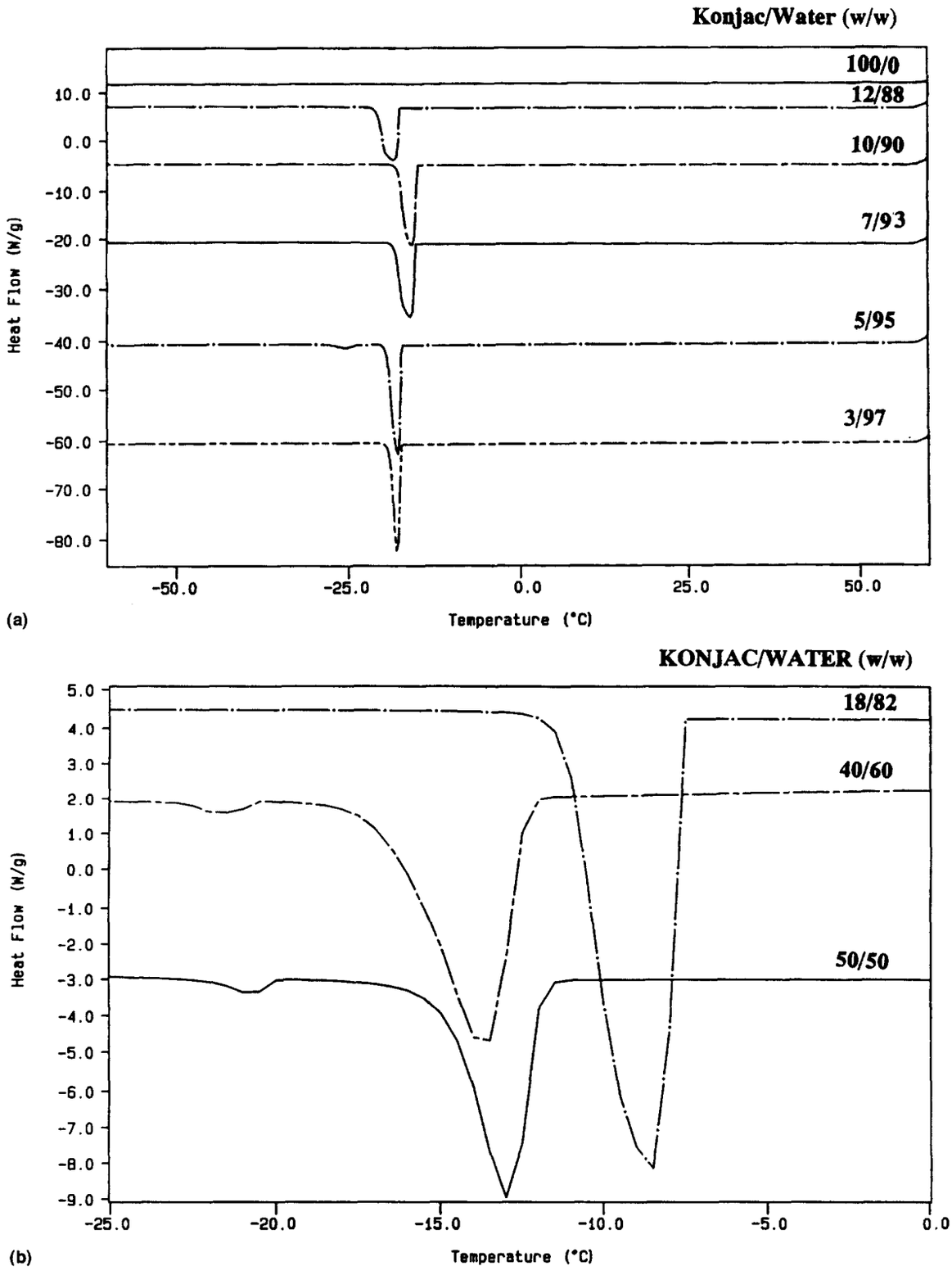


Figure 10 (a) Cooling DSC scans of KGM solutions; (b) Cooling DSC scans of KGM solutions: 18; 40; and 50%

concentration, respectively. If a linear relationship existed between the heat of fusion and % KGM concentration, then at 50% KGM concentration, ΔH values should be about 150 J g^{-1}. However, the experimentally determined value is *ca.* 90 J g^{-1} (i.e. 60 J g^{-1} lower than expected). Therefore, the water molecules that did not crystallize in the frozen phase (approximately 18% based on the linear relationship) represent the non-freezing water which is bound to the KGM backbone. This may be a reason that the rheological properties are independent of processing temperature as the bound water molecules (18%) may act to plasticize the KGM.

Upon cooling, the exotherms which are attributed to the crystallization of water are shaper at the lower KGM concentration [*Figure 10*(a)]. Significant supercooling is observed as the freezing temperature is depressed by 15–20°C. The exotherms shift to lower temperature at higher concentrations and two exotherms are observed upon cooling 40 and 50% KGM concentrations as seen in *Figure 10*(b). The higher and lower exotherms may be

assigned to the freezing of bulk water and associated water with KGM, respectively.

CONCLUSIONS

KGM forms a biphasic LC phase in water at 7% (w/w) concentration and becomes completely anisotropic above 10% (w/w) concentration as observed by polarized optical microscopy. No order–disorder transition was observed when the LC solutions were heated on the hot stage. CD spectra shows positive bands at 210 and 290 nm for the liquid crystalline phase and shear-induced birefringence, respectively. It seems that chemical modification of KGM is required to introduce chromophores to increase the optical signals in order to characterize the LC structure in details. Congo red does not give any induced CD measurement as it does not bind with KGM efficiently. Increases in the intensity of WAXS diffraction pattern of the film cast from LC solutions provided further evidence of the mesophase formation in the KGM solutions.

Viscoelastic measurements does not exhibit a drop in dynamic viscosity after the KGM samples became liquid crystalline possibly due to gelation, which may interfere with the LC phase formation. It seems that KGM form weak gels in water as determined from the G' and G'' measurements, which are dependent on frequency to some extent. Capillary rheometry measurements show that KGM solutions are pseudoplastic and the optimum processing conditions were determined to be independent of temperature. KGM solutions from 30–35% concentration were appropriate from preparing fibres and films as they exhibited preferential orientations determined by WAXS.

DSC analysis of the KGM–water system does not show LC gel–sol transition and is in agreement with the microscopy results. KGM–water samples are not thermoreversible gels as no melting point was observed in the DSC scans. There appears to be some interaction of water with the KGM backbone as non-freezing water exists; this was observed from the heat of enthalpy values. Further investigation is required to confirm this hypothesis.

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